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TOPOLOGICAL ASPECTS OF BENZENOIDS AND CORONOIDS, INCLUDING "SNOWFLAKES" AND "LACEFLOWERS"

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Abstract—A coronoid is a "benzenoid with a hole". Some aspects of the studies of topological properties of benzenoids and coronoids are reviewed. The survey includes the search for concealed non-Kekuléans, multiple zigzag chains and primitive coronoids. Enumerations and classifications of polyhexes (i.e. benzenoids and coronoids) are treated in some details. The original contributions of the present work are concentrated upon polyhexes with hexagonal symmetry.

Benzenoids with hexagonal symmetry are referred to as "snowflakes". The forms of all snowflakes with D_{6h} symmetry and h (the number of hexagons) $\leqslant 55$ are displayed as computer-generated drawings. In addition, the concealed non-Kekuléans with $h = 61$ and $h = 67$ are shown.

Coronoids with hexagonal symmetry represent another main subject of this work. Single coronoids in general are classified into regular including primitive, half essentially disconnected, essentially disconnected and non-Kekuléan systems. The smallest members of all these categories among coronoids with D_{6h} symmetry are displayed, viz. $h \leqslant 36$ for the primitive, $h \leqslant 54$ for the non-Kekuléan systems, and $h \leqslant 30$ for the other categories. Combinatorial formulas of K (the number of Kekulé structures) for some classes of coronoids with hexagonal symmetry are given, including a complete solution for the primitive systems belonging to D_{6h} or C_{6h}.

Finally the forms of the smallest ($h \leqslant 49$) multiple coronoids with D_{6h} symmetry ("laceflowers") are displayed.

1. INTRODUCTION

In the present paper some ideas about benzenoids and coronoids are expanded. Benzenoids were also treated in two papers [1, 2] of the first volume of *Symmetry: Unifying Human Understanding* [3], which may be consulted for precise definitions and for some key references in this topic. Benzenoid systems consist of identical regular hexagons in a plane, while coronoids (also touched upon in one of the cited papers [1]) are, loosely speaking, "benzenoids with a hole". By the term polyhexes we shall refer to the class of benzenoids and coronoids together. Benzenoid systems as mathematical (graph-theoretical) objects have obvious counterparts in benzenoid (polycyclic aromatic) hydrocarbons, which are very well-known in organic chemistry. More than 500 of such compounds have been described in the literature [4], and most of them have been synthesized. It is less-known that two cycloarenes, a new class of polycyclic aromatic hydrocarbons, also have been synthesized, viz. cyclo[*d.e.d.e.d.e.d.e.d.e.d.e*]dodekakisbenzene (kekulene), C_1 [5], and very recently cyclo[*d.e.d.e.e.d.e.d.e.e*]dekakisbenzene, C_2 [6]. These molecules correspond to coronoid systems and are depicted in Fig. 1.

The studies of topological properties of polyhexes have been intensivated during the last years. Even the literature which has appeared after the first volume of *Symmetry* [3] was published is too voluminous to be cited here. We only give the Refs [7–17] to a small portion of the existing relevant papers. All of them are from 1986 or 1987 and tend to represent as many authors as possible. Enumerations and classifications of polyhexes are substantial parts of the recent research in this area; a consolidated report by 14 authors on the present status has appeared [18]. To be precise, this report reflected the situation around the beginning of 1987. During a rapid development in the field a substantial amount of supplementary data is already available.

Enumerations and classifications of polyhexes are also the main subjects of the present paper. It contains some original contributions, which tend to be symmetry-oriented in the sense that emphasis is laid on the most symmetrical systems, i.e. those with hexagonal symmetry.

The numbers of Kekulé structures is an important aspect of polyhexes and will be considered in some details. This topic has been summarized and expanded in a recent book [19].

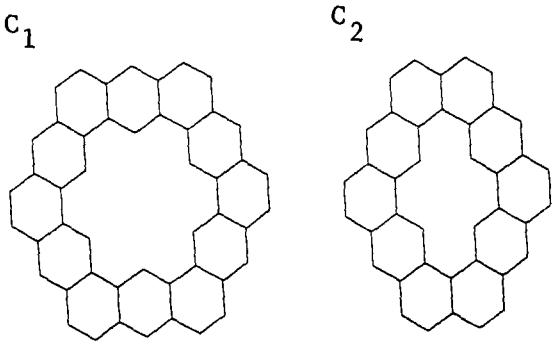


Fig. 1. Two primitive coronoids corresponding to synthesized cycloarenes.

2. EXAMPLES OF THE RESEARCH PROGRESS

Here we summarize some new results in the topological studies of polyhexes in relation to the two contributions [1, 2] in the first volume of *Symmetry* [3]. Some of the terms used in this section are defined more precisely in the subsequent sections. Here we only mention that the number of hexagons in a polyhex is denoted by h and the number of Kekulé structures by K.

Example 2.1

"The two smallest ($h = 11$) non-Kekuléan benzenoids ($K = 0$) with equal number of black and white vertices" [2] is a misleading statement. The category of benzenoids in question is also referred to as concealed non-Kekuléans [20]. It is true that no such systems with less than 11 hexagons exist, but there are more than two of them. The search for smallest concealed non-Kekuléans has continued since Gutman [21] in 1974 published the two frequently quoted forms (see, e.g. Ref. [2]). Finally, in 1986 eight such systems were identified [22]. Still later [23] it was definitely proved by computer enumeration that there exist exactly eight concealed non-Kekuléan systems with $h = 11$ (cf. Fig. 2); therefore any search for more of these systems is futile.

It was also found, according to a private communication from W. He and W. He (Shijiazhuang, China), that there are exactly 98 concealed non-Kekuléans with $h = 12$.

Example 2.2

In the paper [2] commented above it is also stated that the smallest benzenoid with C_{6h} symmetry occurs for $h = 19$, and that only one such system exists. The last part of this statement is wrong. There are exactly two benzenoids with $h = 19$ and C_{6h} symmetry [24]; cf. Fig. 3.

Example 2.3

In the other paper [1] considered here a concealed non-Kekuléan with $h = 43$ and D_{6h} symmetry was depicted (cf. Fig. 4). It was assumed there that this is the smallest system of this category. Later studies [24] have proved that this statement is true. It was deduced by computer enumeration that the system in question is unique, but in addition there are four concealed non-Kekuléans of the same size ($h = 43$) and C_{6h} symmetry; see Fig. 4.

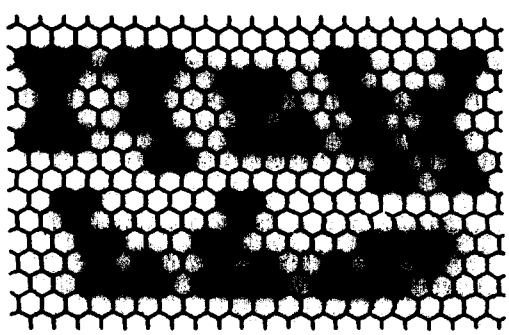


Fig. 2. The eight existing smallest ($h = 11$) concealed non-Kekuléan benzenoids.

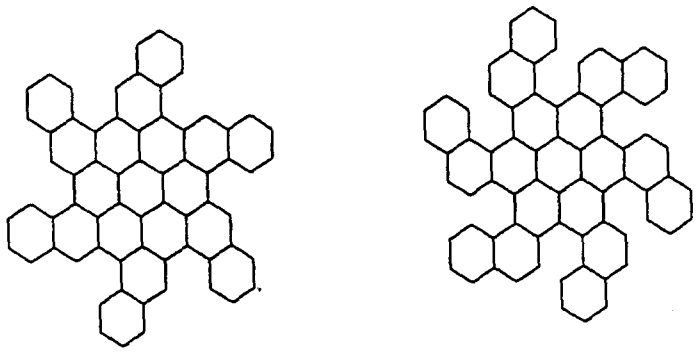


Fig. 3. The two existing smallest ($h = 19$) benzenoids belonging to C_{6h}. The numbers of Kekulé structures (K) are given.

Example 2.4

The benzenoid class of multiple zigzag chains, A(m, n), was treated in some detail in one of the considered papers [2]. The exposition therein, as well as the modest extensions elsewhere [25] have been supplemented with further extensions and qualitatively new findings [16, 19].

For the number of Kekulé structures of A(m, n) with fixed values of n the formulas have not only been extended to $n \leqslant 10$ with the last result:

$$K\{\mathrm{A}(m, 10)\} = \frac{1}{3{,}628{,}800}(m+1)(m+2)(50{,}521m^8 + 606{,}252m^7 + 3{,}221{,}422m^6 + 9{,}895{,}860m^5 + 19{,}220{,}389m^4 + 24{,}175{,}248m^3 + 19{,}240{,}308m^2 + 8{,}866{,}800m + 1{,}814{,}400). \quad (1)$$

Also a general formulation in terms of a determinant was produced, based on the John–Sachs theorem [26]. Instead of giving the general form it seems to be more interesting to give here the application to $n = 10$. Then the below determinant, when expanded properly, is equivalent to the polynomial form (1);

$$K\{\mathrm{A}(m, 10)\} = \begin{vmatrix} \binom{m+2}{2} & \binom{m+3}{4} & \binom{m+4}{6} & \binom{m+5}{8} & \binom{m+6}{10} \\ 1 & \binom{m+2}{2} & \binom{m+3}{4} & \binom{m+4}{6} & \binom{m+5}{8} \\ 0 & 1 & \binom{m+2}{2} & \binom{m+3}{4} & \binom{m+4}{6} \\ 0 & 0 & 1 & \binom{m+2}{2} & \binom{m+3}{4} \\ 0 & 0 & 0 & 1 & \binom{m+2}{2} \end{vmatrix}. \quad (2)$$

Now we pass to the studies of K numbers for A(m, n) with fixed values of m. The recursive properties of these quantities were attacked in a slightly different way from previously [2, 25]

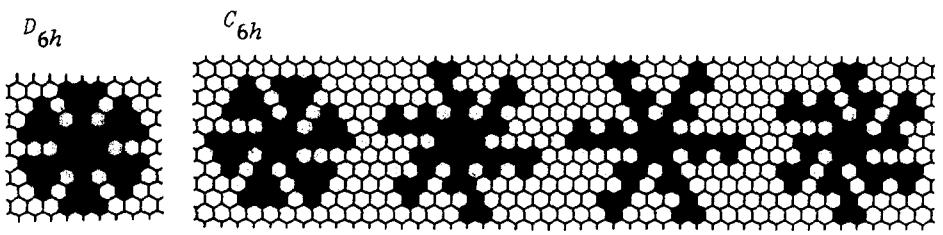


Fig. 4. The five smallest ($h = 43$) concealed non-Kekuléans with hexagonal symmetry.

inasmuch as the n value was allowed to step two units every time. In this new form a general formulation of the recurrence relation was achieved, viz.

$$K\{\mathrm{A}(m, n+2)\} = \sum_{j=0}^{m} (-1)^j \binom{m+j+2}{2j+2} K\{\mathrm{A}(m, n-2j)\}. \tag{3}$$

In spite of these new developments no explicit formula for $K\{\mathrm{A}(m, n)\}$ with fixed values of m is known so far unless $m = 1$.

Example 2.5

A combinatorial K formula for a simple class of so-called primitive coronoids was given [1], kekulene (C_1 of Fig. 1) being one of the members. More extensive studies in this field have been performed, and some more general K formulas have been derived [27, 28].

Consider a cyclic single chain of hexagons with N corners (more precisely: N angularly annelated hexagons) and all the linear segments of equal length. This length is determined by a parameter j, defined so that $h = Nj$. Then

$$K(j, N) = 1 + (-1)^N + 2^{-N}[j + (j^2+4)^{1/2}]^N + 2^{-N}[j - (j^2+4)^{1/2}]^N. \tag{4}$$

For kekulene $N = 6$ and $j = 2$. With these parameters equation (4) reproduces correctly the number of Kekulé structures for kekulene, viz. $K = 200$.

Another class of coronoids is obtained by keeping the number of linear segments constantly six, but allowing for non-equidistant segments. Let their lengths be defined by six (not independent) parameters so that $h = a + b + c + d + e + f$. Then, according to an unpublished result by J. L. Bergan (Trondheim, Norway):

$$K(a, b, c, d, e, f) = abcdef + abcd + bcde + cdef + defa + efab + fabc + ab + bc + cd + de + ef + fa + ad + be + cf + 4. \tag{5}$$

On inserting $a = b = c = d = e = f = j$ for equidistant segments it is obtained

$$K(j) = (j^3 + 3j)^2 + 4 = (j^2+1)^2(j^2+4), \tag{6}$$

and finally for kekulene: $K(2) = 200$.

3. SOME DEFINITIONS AND THE INVARIANT Δ

The characteristic number (or invariant) Δ for a polyhex plays an important role in the topology of polyhexes. It is a positive integer or zero.

Throughout this paper we assume that a polyhex, P, is drawn (as usually) so that some of its edges are vertical. Let the n vertices of P be colored alternately black and white. The numbers of the colored vertices are $n^{(b)}$ and $n^{(w)}$, respectively. The peaks (p) and valleys (v) are the vertices on the circumference (perimeter) which point upwards and downwards, respectively. We adopt the convention that all peaks are white, and therefore all valleys black. Furthermore, if $n^{(b)} \neq n^{(w)}$, we assume as another convention $n^{(b)} > n^{(w)}$.

The invariant Δ is defined by

$$\Delta = n^{(b)} - n^{(w)}. \tag{7}$$

It has been pointed out [2] that also

$$\Delta = n_i^{(b)} - n_i^{(w)}, \tag{8}$$

where the difference is taken between the numbers of black and white internal vertices only. This feature is easily understood by the fact that the external vertices (which constitute the perimeter) consist of an equal number of black and white vertices. Hence they may be deleted as indicated in Fig. 5, whereby the counting for Δ is facilitated. A third way to determine Δ is often the easiest one, namely by taking the difference between the numbers of valleys and peaks, viz.

$$\Delta = n_v - n_p. \tag{9}$$

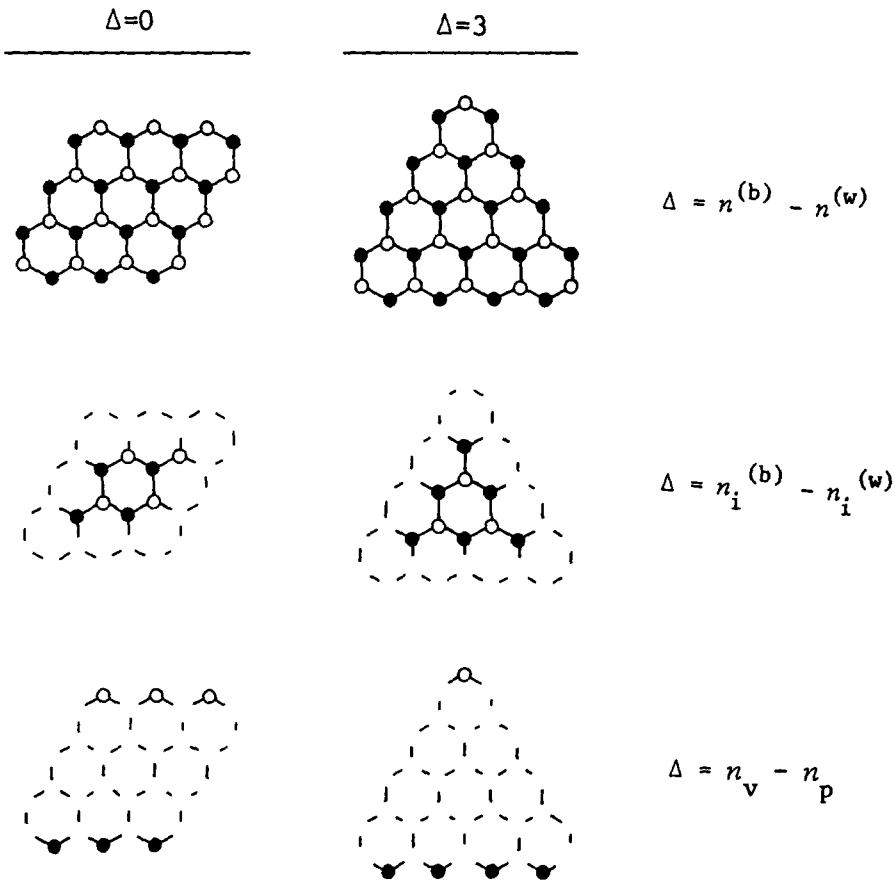


Fig. 5. Colored vertices and Δ values for two benzenoids: anthanthrene (left column) with Δ = 0, a Kekuléan system; triangulene (right column) with Δ = 2, an obvious non-Kekuléan system.

Figure 5 explains this feature; in the bottom figures all vertices belonging to vertical edges are deleted, leaving only the peaks and valleys. Again it is clear that an equal number of black and white vertices was deleted. This proof of equation (9) is due to W. He and W. He according to a private communication. A more complicated proof was earlier conducted by Cyvin and Gutman [20]. It should be noted that the absolute numbers of peaks and valleys depend on the chosen orientation of P, but the difference (9) is invariant.

4. FURTHER DEFINITIONS AND THE "*neo*" CLASSIFICATION

4.1. Definitions

A polyhex is said to be Kekuléan when it possesses Kekulé structures ($K > 0$) and non-Kekuléan when it does not possess any Kekulé structure ($K = 0$). All Kekuléan systems are known to have $\Delta = 0$, but this is not a sufficient condition for being Kekuléan. Systems with $K = 0$ and $\Delta = 0$ exist and are referred to as concealed non-Kekuléan (cf. e.g., Figs 2 and 4). The other non-Kekuléans ($K = 0$, $\Delta > 0$) are called obvious.

Catacondensed polyhexes are those which have no vertex shared by three hexagons. When formulated in this way the definition applies to both benzenoids and coronoids. For benzenoids the catacondensed systems are often defined by the absence of internal vertices. All catacondensed polyhexes are known to be Kekuléan. Polyhexes which are not catacondensed are said to be pericondensed.

Some polyhexes among the pericondensed Kekuléan systems are designated essentially disconnected. They are defined by the presence of fixed bonds (i.e. single or double) in certain positions in all Kekulé structures. In essentially disconnected systems the total number of Kekulé structures

is given by the product of K numbers for two or more subunits, which behave independently with regard to the Kekulé structures. These subunits are referred to as the effective units.

Kekuléan polyhexes which are not essentially disconnected are said to be normal.

4.2. Kekulé structures of normal benzenoids

The distinction between normal and essentially disconnected benzenoids among the Kekuléans is very important in the theory of Kekulé structure counts. There are infinitely many essentially disconnected benzenoids with $K = 9$ and any other possible (not arbitrary) value $K > 9$. In sharp contrast, the number of normal benzenoids with any $K > 1$ is limited. This statement is a corollary of a recently proved theorem [29]: For a normal benzenoid with h hexagons the minimum number of Kekulé structures is

$$K_{\min}(h) = h + 1. \tag{10}$$

This minimum K number is realized in exactly one system for a given h, namely the linear single chain (polyacene). The K numbers of normal benzenoids have also otherwise been studied extensively under the keywords "distribution of K" and "Kekulé structure statistics" [30–34]. In consequence of the above discussion it is sensible to ask: How many normal benzenoids have K (any integer $K > 1$) Kekulé structures? The answer is, for instance, 3, 12, 32, 54, 97, 150, 176, 256, 468 and 444 for $K = 10, 20, \ldots, 90$ and 100, respectively (from Ref. [32] and unpublished results). In addition to the lower limit (10) of K for normal benzenoids also the maximum values have been studied [30, 34, 35]. For $h = 1, 2, \ldots, 9$ and 10 one has $K_{\max}(h) = 2, 3, 5, 9, 14, 24, 41, 66, 110$ and 189, respectively. One of the results for an upper bound on K is:

$$K_{\max}(h) \leqslant 3^{h/2}; \quad h > 1. \tag{11}$$

This gives a constant upper bound for the quantity $(\ln K_{\max})/h$, which is related to the resonance energy of the benzenoid [2, 36]. We have found that this quantity also has a lower limit:

$$\tfrac{1}{3}[\ln(5 + 17^{1/2}) - \ln 2] < \frac{1}{h} \ln K_{\max}(h) \leqslant \tfrac{1}{2} \ln 3; \quad h > 1. \tag{12}$$

Here the sign of equality is valid for $h = 2$ and $h = 4$, only.

4.3. The "neo" classification

In conclusion of this chapter we define the *neo* classification, which takes account of all benzenoids. They are either normal (n), essentially disconnected (e) or non-Kekuléan (o).

Figure 3 shows two normal benzenoids with hexagonal symmetry. Some (concealed) non-Kekuléans are shown in Figs 2 and 4, the latter ones (Fig. 4) having hexagonal symmetry. Figure 5 contains a normal benzenoid (left) and an (obvious) non-Kekuléan (right). In supplement of these examples we show (Fig. 6) the two smallest essentially disconnected benzenoids with hexagonal symmetry.

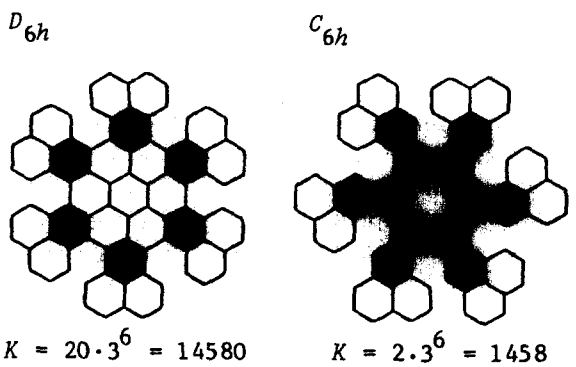


Fig. 6. The two smallest ($h = 25$) essentially disconnected benzenoids with hexagonal symmetry (D_{6h} and C_{6h}). The effective units are white. K numbers are given.

5. ENUMERATION AND CLASSIFICATION OF BENZENOIDS WITH HEXAGONAL SYMMETRY

The benzenoids with hexagonal symmetry (D_{6h} and C_{6h}) are very sparsely distributed among the totality of the systems. Among the 849,285 benzenoids with $h \leqslant 12$ there are only two systems with hexagonal symmetry, viz. benzene ($h = 1$) and coronene ($h = 7$); cf. Table 1 [18, 24, 37]. Therefore it would be hopeless to continue more extensive enumerations of the benzenoids with hexagonal symmetry as a subset of the total amount. Fortunately this is not necessary inasmuch as the systems of interest may be generated specifically by computer-aided procedures [24]. In Table 1 the listing for the two symmetry groups in question goes far beyond $h = 12$.

The benzenoids with hexagonal symmetry have been referred to as "snowflakes" [1, 38]. The reason for this is obvious from the treatise in another book on *Symmetry* [39]. However, the designation is most appropriate for the systems of D_{6h} symmetry (and not C_{6h}). Nevertheless it seems practical to use the term "snowflakes" for both symmetry groups. When we wish to distinguish between them we shall use the terms "proper" and "improper" snowflakes for D_{6h} and C_{6h}, respectively.

The values of h, the number of hexagons, for all snowflakes are discrete according to:

$$h = 6\eta + 1; \quad \eta = 0, 1, 2, \ldots . \tag{13}$$

Table 1. Benzenoids enumerated and classified according the the *neo* classification

h	Class†	D_{6h}	C_{6h}	Other symmetries	h	Class†	D_{6h}	C_{6h}
1	*n*	1	0	0	13	*n*	2	0
2	*n*	0	0	1	19	*n*	2	2
3	*n*	0	0	2	25	*n*	2	7
	o	0	0	1		*e*	1	1
4	*n*	0	0	6	31	*n*	5	24
	o	0	0	1		*e*	0	8
5	*n*	0	0	14	37	*n*	7	84
	e	0	0	1		*e*	1	44
	o	0	0	7				
					43	*n*	11	310
6	*n*	0	0	48		*e*	1	213
	e	0	0	3		*o*	1	4
	o	0	0	30				
					49	*n*	17	{2167
7	*n*	1	0	166		*e*	3	
	e	0	0	23		*o*	0	42
	o	0	0	141				
					55	*n*	30	{9158
8	*n*	0	0	643		*e*	4	
	e	0	0	121		*o*	1	312
	o	0	0	671				
					61	*n*	{59	
9	*n*	0	0	2531		*e*		
	e	0	0	692		*o*	1	
	o	0	0	3282				
					67	*n*	{100	
10	*n*	0	0	10375		*e*		
	e	0	0	3732		*o*	4	
	o	0	0	15979				
					73	*n*	{176	
11	*n*	0	0	42919		*e*		
	e	0	0	19960		*o*	7	
	o	0	0	78350				
12	*n*	0	0	{284918				
	e	0	0					
	o	0	0	384666				

†Abbreviations: *n*—normal; *e*—essentially disconnected; *o*—non-Kekuléan.

Data for $h \leqslant 11$ see Ref. [18] and the references cited therein. The entries for $h = 12$ are based on a private communication from W. He and W. He (Shijiazhuang, China). For the systems of hexagonal symmetries and $13 \leqslant h \leqslant 55$, see Refs [18, 24, 37]. The data for $h > 55$ are present results.

Here $\eta = 0$ pertains to benzene, a trivial snowflake. Otherwise ($\eta > 0$) all snowflakes are pericondensed: coronene ($\eta = 1$) and systems with coronene as a subunit. It is also an interesting fact that all snowflakes have $\Delta = 0$. Hence there are no obvious non-Kekuléans among them. Yet non-Kekuléan snowflakes exist (see, e.g. Fig. 4); they are all concealed non-Kekuléans.

All the existing snowflakes up to $h = 37$ have been depicted elsewhere [24], as well as selected examples for $h = 43$ [24]. An account of the non-Kekuléans with $h = 49$ is to be published, as well as selected non-Kekuléans with $h = 55$ [37].

In the present work we have pursued the enumeration of proper snowflakes, mainly because of the aestethical values. Here the D_{6h} systems are for the first time generated specifically. Figure 7 shows all the 90 systems with $h \leqslant 55$ in terms of computer-designed pictures. There are only two concealed non-Kekuléans among them. We have also identified the concealed non-Kekuléan proper snowflakes beyond $h = 55$, actually up to $h = 73$. The result is displayed in Fig. 8.

6. ANALYSING SINGLE CORONOIDS: THE "*rheo*" AND "*rio*" CLASSIFICATIONS

6.1. Introduction

The definitions of Section 4.1 apply to coronoids as well as benzenoids. We give at once (Fig. 9) two examples of essentially disconnected coronoids among the systems with hexagonal symmetry. Also the *neo* classification is applicable to coronoids. Table 2 [18, 40, 41] shows the results of enumeration of coronoids with special emphasis on those with hexagonal symmetry. They are classified according to *neo*.

It became soon clear that the K numbers "misbehave" within the class of normal coronoids. The root of this problem seems to be the lack of a specific generation procedure for normal polyhexes

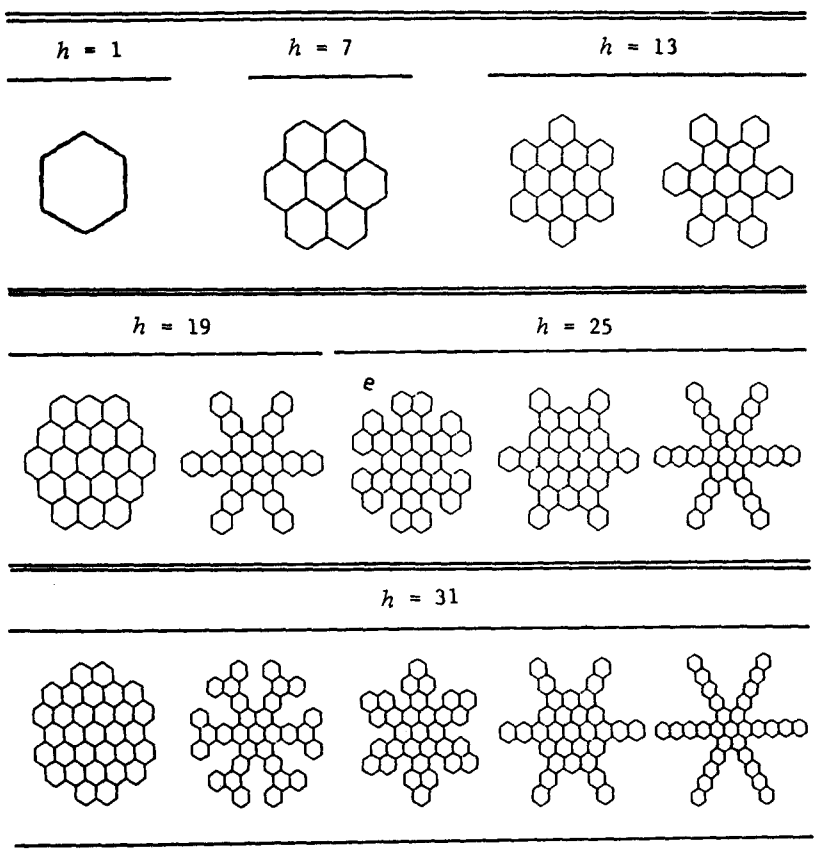


Fig. 7a

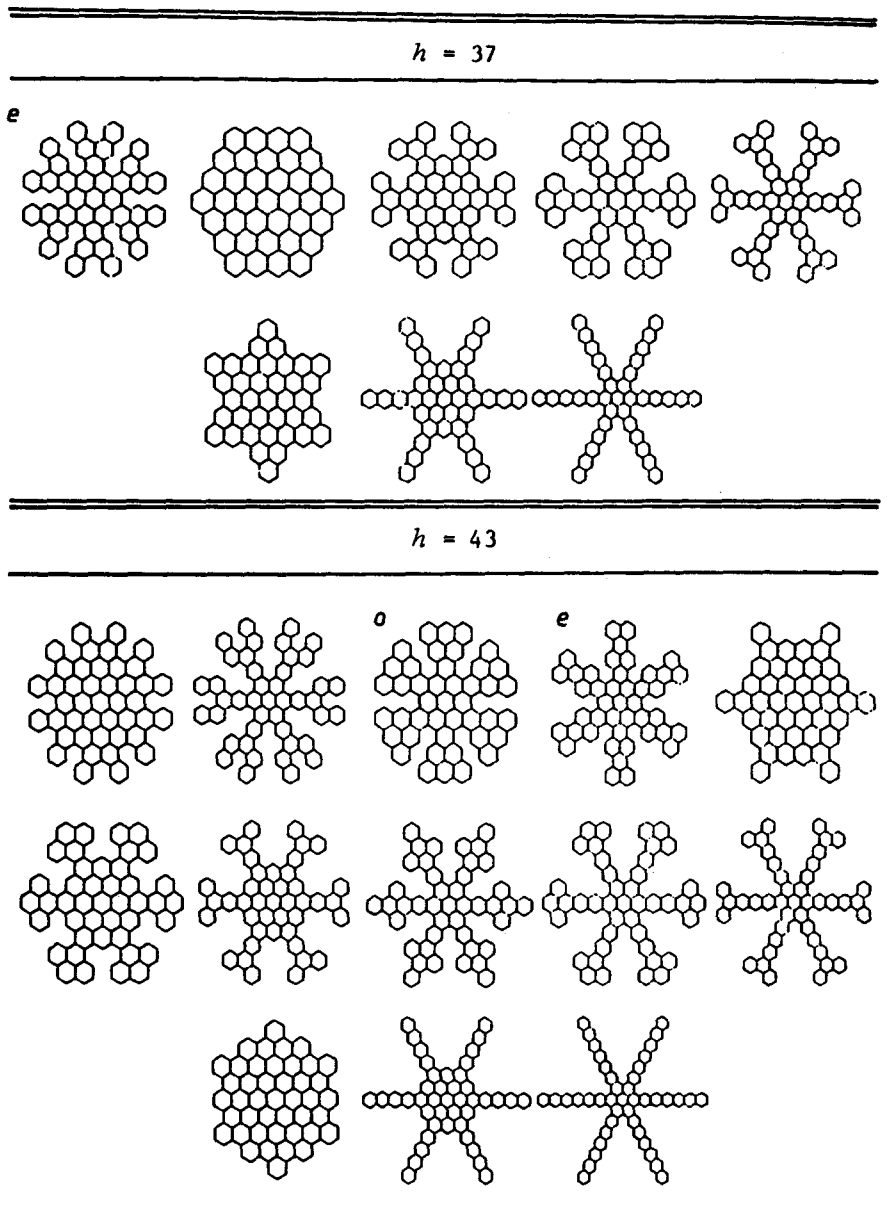


Fig. 7b

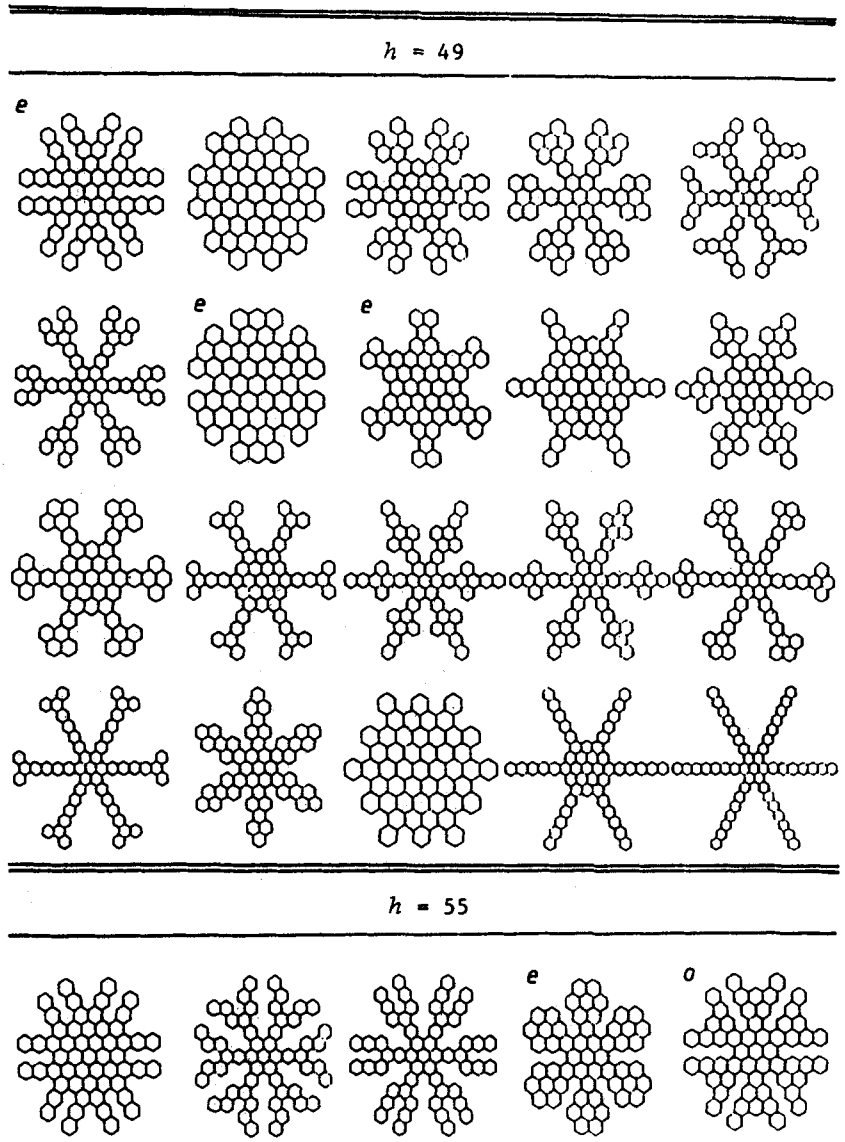


Fig. 7c

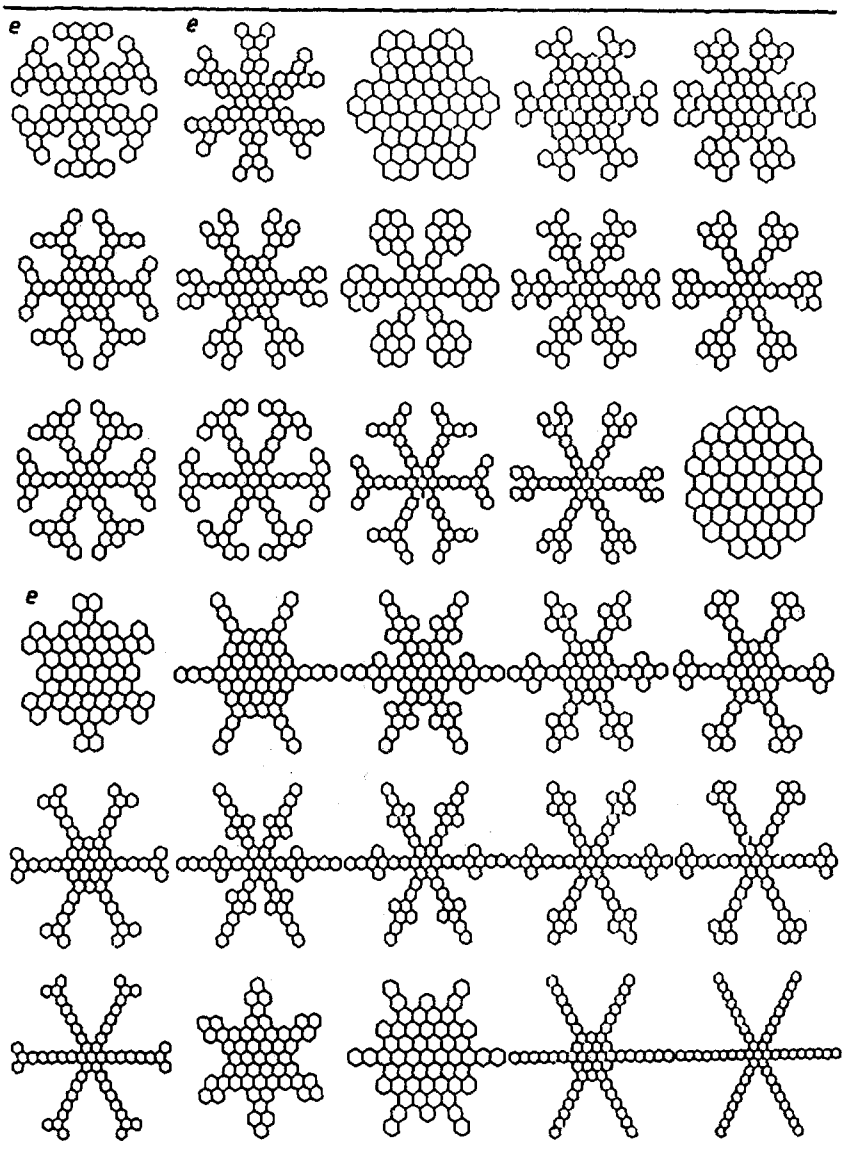


Fig. 7d

Fig. 7. Computer-generated "proper snowflakes" (benzenoids of symmetry D_{6h}) for $1 \leqslant h \leqslant 55$. Abbreviations: *e* essentially disconnected; *o* (concealed) non-Kekuléan. All others are normal (Kekuléan).

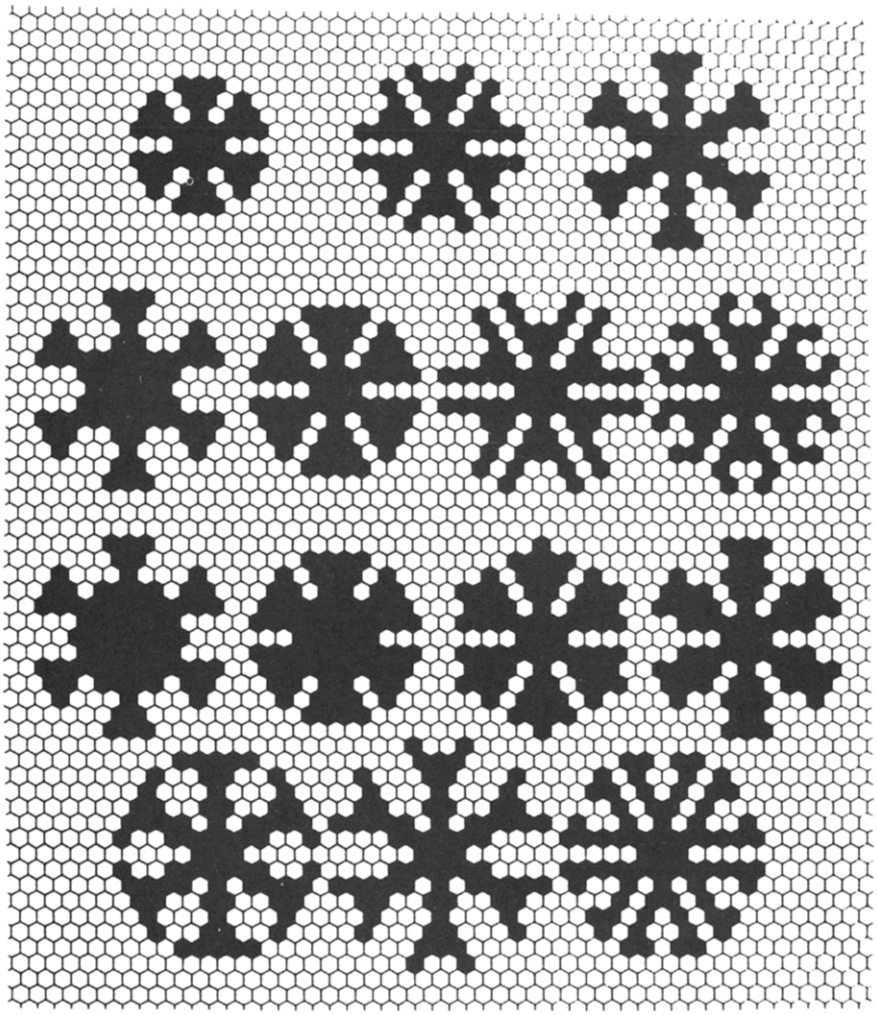


Fig. 8. All concealed non-Kekuléan proper snowflakes with $h \leqslant 73$: one system each with $h = 43$, 55 and 61, four systems with $h = 67$, and seven systems with $h = 73$.

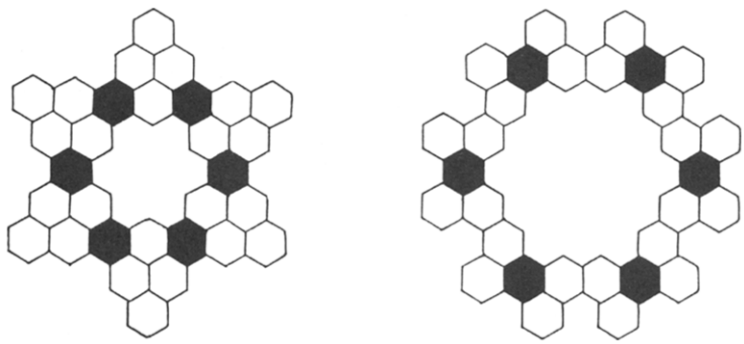


Fig. 9. The two smallest ($h = 30$) essentially disconnected coronoids with D_{6h} symmetry. The effective units are white. K numbers are given.

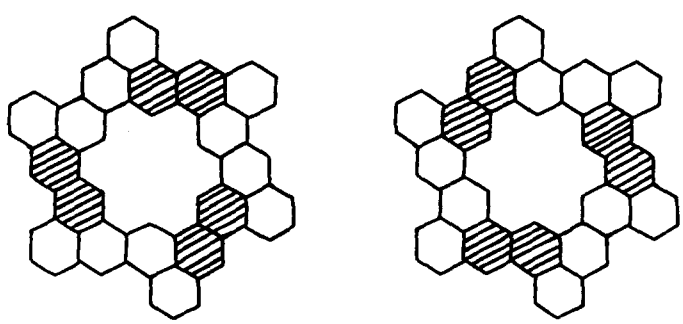
Table 2. Coronoids enumerated and classified according to the *neo* classification

h	Class†	D_{6h}	C_{6h}	Other symmetries	h	Class†	D_{6h}	C_{6h}
8	*n*	0	0	1	18	*n*	3	1
9	*n*	0	0	3	24	*n*	9	7
	o	0	0	2				
					30	*n*	18	41
10	*n*	0	0	24		*e*	2	3
	o	0	0	19				
					36	*n*	43	192
11	*n*	0	0	126		*e*	4	33
	e	0	0	2				
	o	0	0	155	42	*n*	} 97	} 1113
						e		
12	*n*	1	0	819				
	e	0	0	34	48	*n*	} 221	
	o	0	0	1100		*e*		
						o	1	
13	*n*	0	0	} 5050				
	e	0	0		54	*n*	} 456	
	o	0	0	7313		*e*		
						o	3	
					60	*n*	} 1009	
						e		
						o	20	

†See footnote to Table 1.
Data for $h \leqslant 12$, see Ref. [18] and references cited therein. The entries for $h \geqslant 13$ are from Refs [18, 40, 41], supplemented with present results.

(when coronoids are included). For normal benzenoids every system with $h + 1$ hexagons, say B_{h+1}, may be generated from a system with h hexagons, B_h, which also is a normal benzenoid. It is known that such a $B_h \rightarrow B_{h+1}$ addition (referred to as a normal addition [19, 41]) invariably makes the K number increase: $K\{B_{h+1}\} > K\{B_h\}$.

The distinguishing of "half essentially disconnected" (HED) coronoids [41] among the normal systems seems to give a remedy for the misbehaviour of K numbers as far as the single coronoids (with exactly one hole) are concerned. A HED coronoid possesses two schemes for its Kekulé structures; the set belonging to one scheme has edges with fixed bonds (single or double) in certain positions. An example is shown in Fig. 10. This characteristic feature, however, is not sufficient as a definition of the HED systems. So far this question has not been fully clarified. In fact only one short communication where the idea of HED coronoids was launched, has appeared. The best approach seems to be to start with a definition of "regular" polyhexes in terms of a generation procedure $P_h \rightarrow P_{h+1}$ (so-called regular addition [41]). When properly defined this procedure generates (a) all normal benzenoids and (b) a subset of normal coronoids which are not half essentially disconnected. The latter class (b) is referred to as "regular" coronoids. Hence the HED



$K = 2 \cdot 7^3 = 686$

Fig. 10. The smallest ($h = 18$) HED coronoid with hexagonal symmetry (C_{6h}). The two (symmetrically equivalent) schemes for Kekulé structures are shown, and the K number is given.

coronoids could be defined as the Kekuléan systems which are neither regular or essentially disconnected.

The four categories regular (r), half essentially disconnected ($\frac{1}{2}e$), essentially disconnected (e) and non-Kekuléan (o) seem to cover all single coronoids, although no strict proof has been given to this effect. The *rheo* classification refers to these four categories. It is also practical to define the class of "irregular" coronoids as those which are Kekuléan and not regular. The *rio* classification refers to the categories regular (r), irregular (i) and non-Kekuléan (o).

A survey of the different classes of coronoids:

$$\text{normal } (n)\begin{cases}\text{regular } (r)\\ \left.\begin{array}{l}\text{half essentially disconnected } (\frac{1}{2}e)\\ \text{essentially disconnected } (e)\end{array}\right\}\text{irregular } (i)\\ \text{non-Kekuléan } (o).\end{cases}$$

Here we shall not go further into more precise definitions of the coronoid classes (or categories), but give some examples from computer-aided enumerations of coronoids with hexagonal symmetry.

All single coronoids with the symmetries D_{6h} and C_{6h} have a hole of the shape of coronene or larger. The number of hexagons is

$$h = 6\eta; \quad \eta = 2, 3, 4, \ldots. \tag{14}$$

Here $\eta = 2$ pertains to kekulene (C_1 of Fig. 1). All these systems have $\Delta = 0$, as also is the case for the benzenoids with hexagonal symmetry (cf. Section 5).

The present examples are restricted to the coronoids of D_{6h} symmetry ("proper snowflakes with a hole"). Figure 11 shows systems of primitive coronoids; they are defined as consisting of one (circular) single chain of hexagons. All primitive coronoids are regular. The other (non-primitive) regular coronoids for some of the lowest h values are found in Fig. 12. The smallest HED coronoid

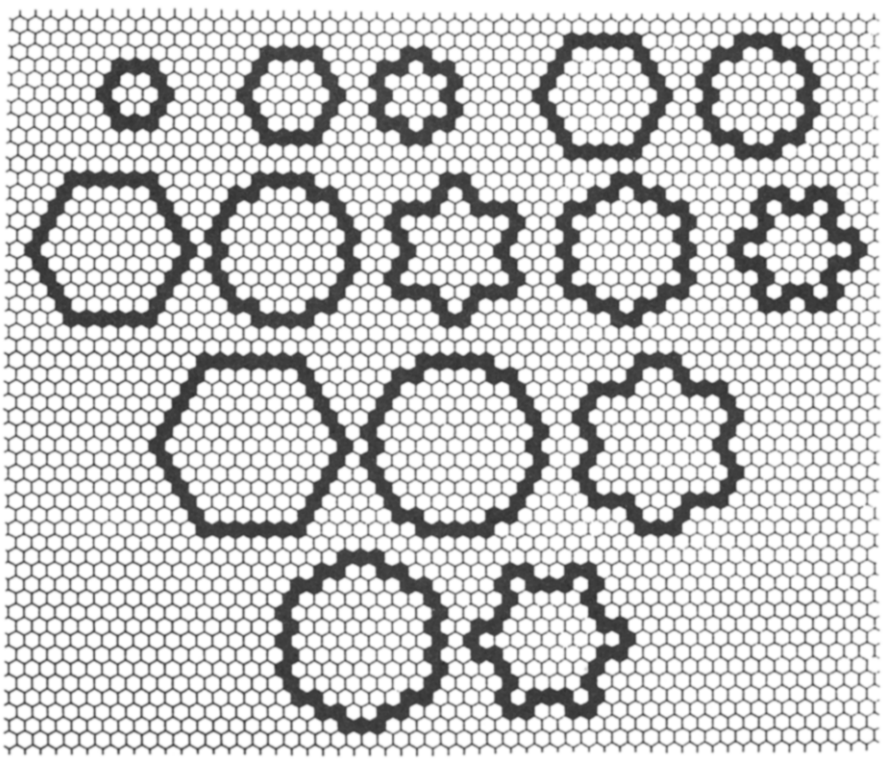


Fig. 11. All primitive coronoids of D_{6h} symmetry and $h \leqslant 36$: one system with $h = 12$, two each with $h = 18$ and 24, and five each with $h = 30$ and 36. The K numbers are: 200; 1300, 5780; 5780, 54,760; 19,604, 287,300, 571,540, [1,860,500, 1,860,500]; 54,760, 1,060,904, 7,761,800, [17,172,740, 17,172,740]. The bracketed figures pertain to isoarithmic systems.

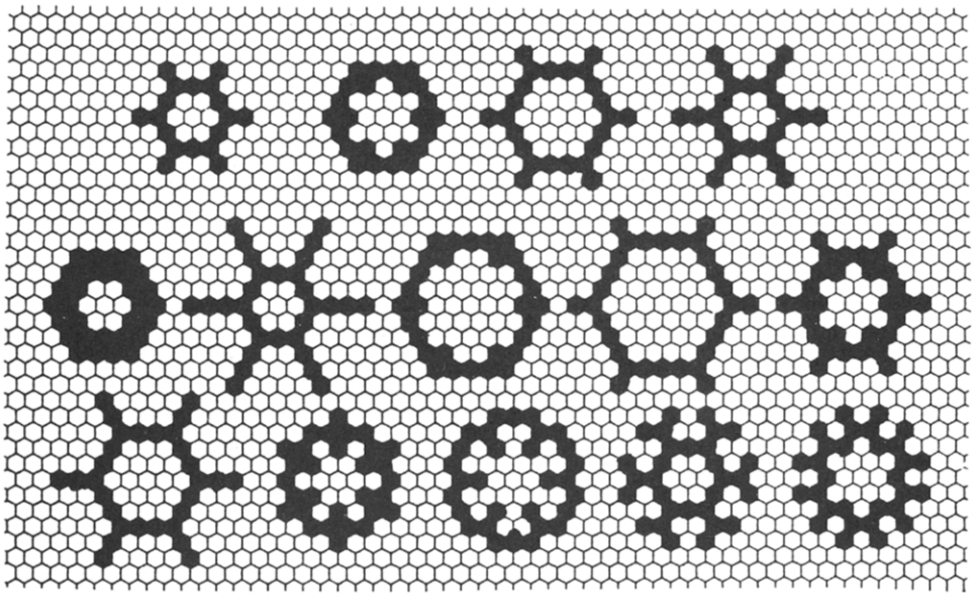


Fig. 12. All non-primitive regular coronoids of D_{6h} symmetry and $h \leqslant 30$: one system with $h = 18$, three with $h = 24$, and ten with $h = 30$. The K numbers are: 7776; 10,108, 63,536, 73,008; 27,508, 36,992, 73,008, 313,632, 497,664, 656,208, 1,060,904, 1,123,632, 2,592,000, 3,504,640.

of hexagonal symmetry belongs to C_{6h}; see Fig. 10. The smallest systems of this kind belonging to D_{6h} are shown in Fig. 13. We refer to Fig. 9 for the two smallest essentially disconnected coronoids belonging to D_{6h}. Finally we show some of the smallest non-Kekuléan coronoids of D_{6h} symmetry. They are all concealed non-Kekuléans. The reported numbers in Figs 9–14 are consistent with the data of Table 2.

7. COMBINATORIAL K FORMULAS FOR CLASSES OF SOME CORONOIDS WITH HEXAGONAL SYMMETRY

7.1. Primitive coronoids

Some primitive coronoids of hexagonal symmetry are members of the classes covered by equations (4) or (6) with respect to their numbers of Kekulé structures (K).

Here we give a quite general result for the K number of a primitive coronoid of hexagonal symmetry:

$$K = (u_0^2 + 2u_0u_3 + u_3^2 + 1)^2(u_0^2 + 2u_0u_3 + u_3^2 + 4) = (u_0 + u_3)^6 + 6(u_0 + u_3)^4 + 9(u_0 + u_3)^2 + 4. \quad (15)$$

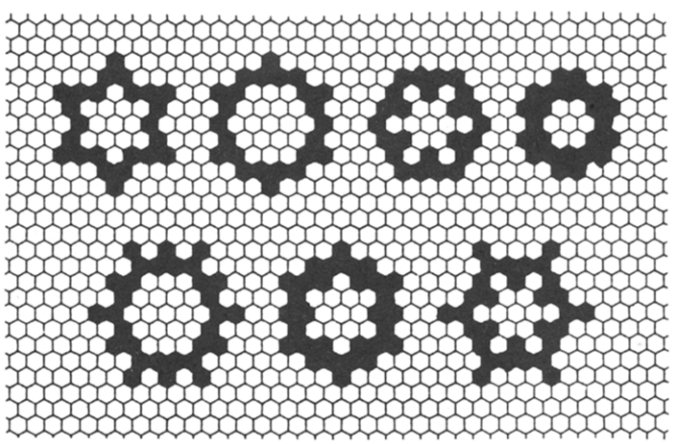


Fig. 13. The smallest HED coronoids belonging to D_{6h}: four systems with $h = 24$ and three with $h = 30$. The K numbers are: 2000, 4394, 4394, 11,664; 21,296, 148,176, 170,368.

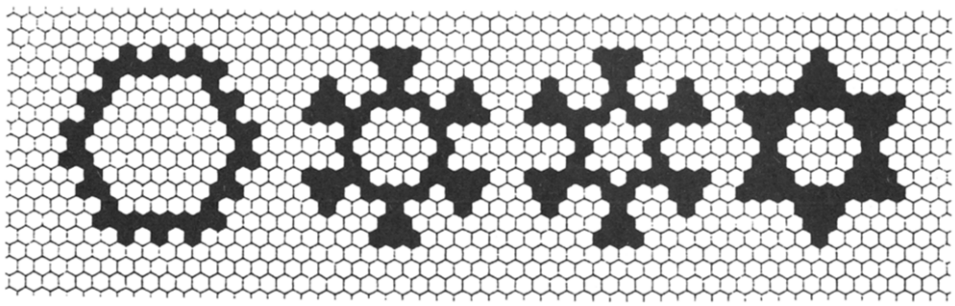


Fig. 14. The smallest concealed non-Kekuléan coronoids belonging to D_{6h}: one system with $h = 48$ and three with $h = 54$.

An algorithm for the quantities u_0 and u_3, along with U, u_1 and u_2, is given in the following:

1. Choose two symmetrically equivalent corners (A hexagons) generated by a rotation of 60°.
2. Depict the single chain from A to A inclusive, and call it U.
3. Delete the two end hexagons (A) to produce u_0.
4. Delete one end hexagon and the linear segment at the other end in the two different ways; call the fragments u_1 and u_2.
5. Delete both linear end segments to produce u_3.

Figure 15 illustrates this algorithm for two choices pertaining to the system with $K = 571{,}540$ in Fig. 11.

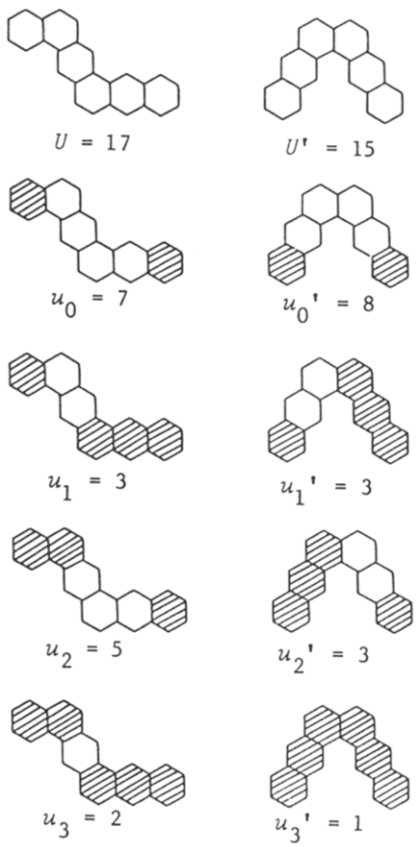


Fig. 15. Two catacondensed unbranched benzenoids, U (single chains), and their fragments u_i ($i = 0, 1, 2, 3$), represented by the unhatched parts. K numbers are given. The bottom-right drawing exemplifies the degenerate case of no hexagons with $K = u_3' = 1$. Notice:

$$\begin{vmatrix} 7 & 3 \\ 5 & 2 \end{vmatrix} = \begin{vmatrix} 8 & 3 \\ 3 & 1 \end{vmatrix} = -1.$$

Let the K numbers of U and its fragments be denoted $K\{U\} = U$ and $K\{u_i\} = u_i$ $(i = 0, 1, 2, 3)$. One has

$$U = u_0 + u_1 + u_2 + u_3 \tag{16}$$

as a simple deduction from the method of fragmentation [42]. A more interesting theorem is (for numerical examples, see Fig. 15):

$$\begin{vmatrix} u_0 & u_1 \\ u_2 & u_3 \end{vmatrix} = u_0 u_3 - u_1 u_2 = -1. \tag{17}$$

The formula for K (15) was deduced by means of a symmetry-adapted method of fragmentation (SAMF) [38, 40, 43, 44]. In our example, notice that $u_0 + u_3 = u_0' + u_3' = 9$. On inserting this value into equation (15) one obtains correctly $K = 571{,}540$.

7.2. Classes of HED coronoids

Two classes of HED coronoids, each determined by two parameters (j, m), are depicted in Fig. 16. The example of Fig. 10 is a member of both classes. Combinatorial K formulas for the special cases with $j = 2$ of the two classes in question have been given previously [40], as determined by SAMF. On realizing that the members are HED coronoids we are able to derive such combinatorial formulas appreciably easier. In the present cases

$$K = 2E^3, \tag{18}$$

where E is the number of Kekulé structures for the pertinent effective unit (cf. Fig. 16), a single chain of three segments (for a general K formula pertaining to this unbranched single chain, see, e.g. Ref. [19]).

7.3. A class of regular coronoids

Finally in this section we give a two-parameter K formula for a class of regular coronoids; see Fig. 17. The special cases of $m = 2$ (j arbitrary) and $j = 2$ (m arbitrary) have been treated previously [38, 40]. The formula in Fig. 17, which was derived by SAMF, is a generalization of the previous findings.

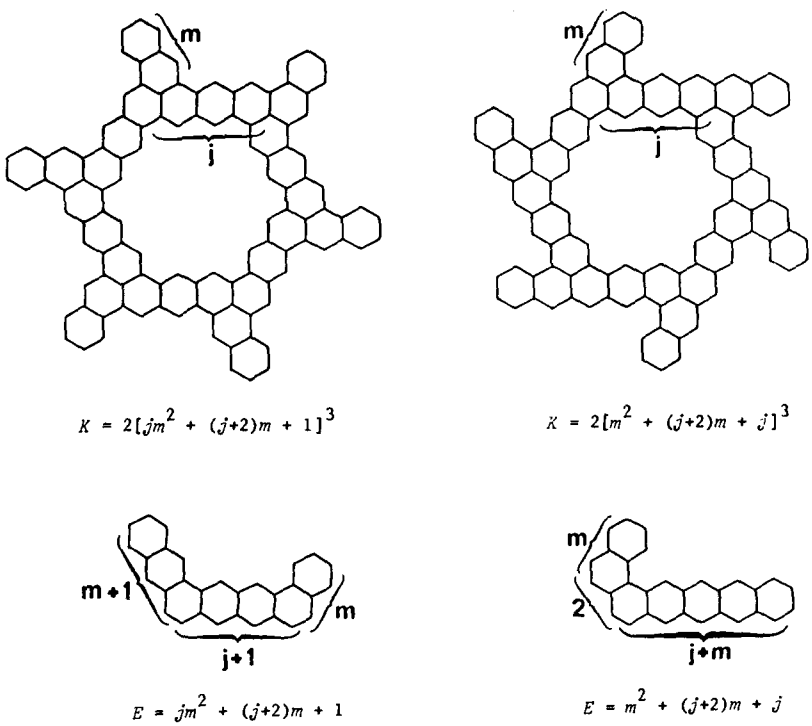
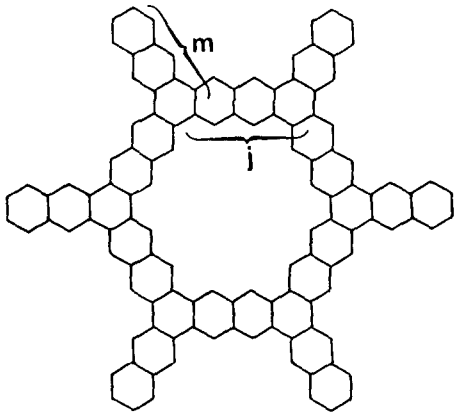


Fig. 16. Two classes of HED coronoids with the corresponding combinatorial K formulas. Also the K formulas for the effective units (E) are given.



$$K = m^3(j^6m^3 + 6j^4m^2 + 9j^2m + 4)$$

Fig. 17. A class of regular coronoids. The K formula is given.

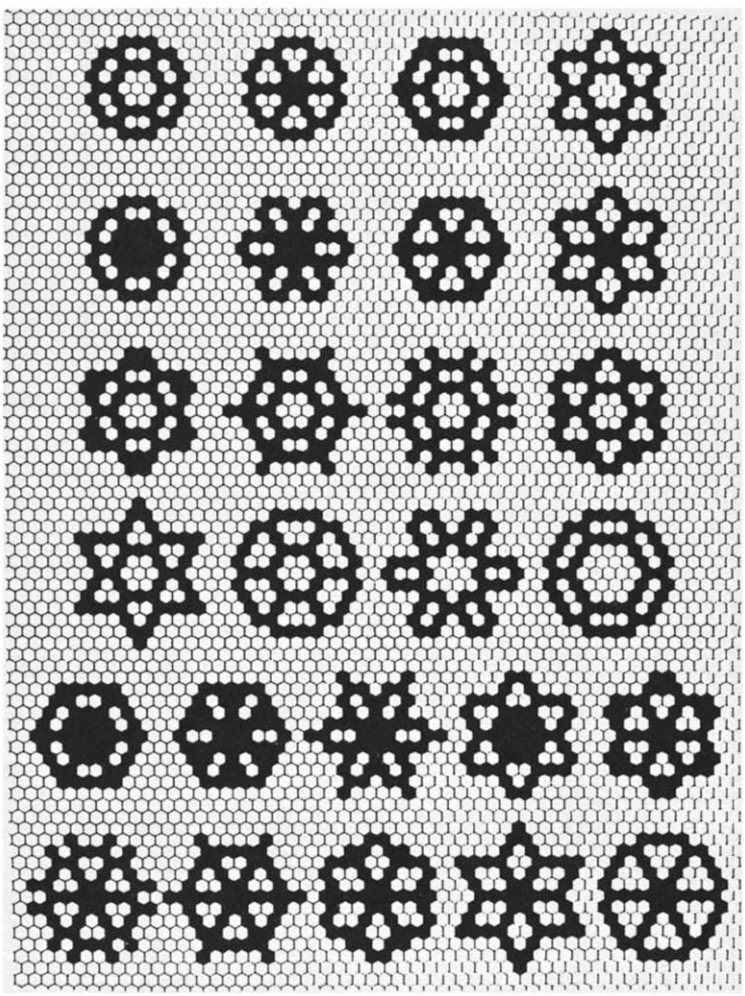


Fig. 18. All laceflowers of D_{6h} symmetry and $h \leqslant 49$: one system with $h = 36$ and $h = 37$, two with $h = 42$, four with $h = 43$, eight with $h = 48$ and ten with $h = 49$.

8. MULTIPLE CORONOIDS WITH HEXAGONAL SYMMETRY

The classification of multiple coronoids (i.e. those with more than one hole) seems to be a large problem and has so far not been solved in a satisfactory way. Only as a fragmentary result Cyvin *et al.* [41] demonstrated four schemes for Kekulé structures of a double coronoid (two holes), which properly could be termed "one quarter essentially disconnected".

A multiple coronoid with hexagonal symmetry has at least six holes. We have coined the term "laceflowers" for these systems.

All the smallest ($h \leqslant 49$) laceflowers with regular hexagonal (D_{6h}) symmetry were first derived by hand. Later the completeness of this analysis was confirmed by generating exactly the same pretty systems (Fig. 18) with computer aid.

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